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Dynamical Properties of ⁵⁷Fe Dissolved in Al Observed by Mössbauer Effect

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The Mössbauer effect of ⁵⁷Fe in aluminum was measured over the temperature range 20–642 °C, using a source specimen of aluminum with ⁵⁷Co in solid solution. The line-broadening values were converted to diffusion constants, which can be expressed by the temperature dependence $D = 0.12 e^{-(1.4 \text{ eV})/kT} \text{ cm}^2/\text{sec}$. This result differs from recent diffusion-constant determinations obtained by the tracer-sectioning method, which we feel might be in error because of solution trapping. From theoretical considerations we suggest that a new expression for the correlation factor for the diffusional line broadening might be more accurate than the one used heretofore. Earlier determinations of the second-order Doppler shift were extended almost to the melting point of aluminum. The shift depends almost linearly on temperature, with the slope given by the Dulong–Petit rule for the heat capacity. From the temperature dependence of the Lamb–Mössbauer factor an effective Debye temperature of $(210 \pm 15)^\circ\text{K}$ was found.

I. INTRODUCTION

The limit of solid solubility of iron in fcc metallic aluminum¹ is about 0.025 at.%. Because of this extremely small solubility, the solid-solution phase coexists with a clustered phase, except when the concentration is very small. The clustered state is of a complicated structure whose approximate composition² can be represented by Fe₄Al₁₃.

There is agreement between a number of experimental workers that the solid-solution phase, which undoubtedly is substitutional, gives a single unbroadened line in the Mössbauer spectrum, while the Fe₄Al₁₃ signal is a broad line with little structure. Bush, Stickels, and Hobbs³ investigated the effects of cold work and heat treatment on quenched samples. Janot and Lelay⁴ made similar studies of the effects of cold work on dilute alloys of iron in aluminum. Nasu and co-workers^{5,6} measured the shift of the solid-solution line as a function of temperature up to 450 °K, and from this they separated the thermal and the isomer shifts from each other. Preston and Gerlach⁷ used a specimen containing iron partly in the clustered state. They separated the overlapping signals

from the two phases by computer fitting and thus obtained data up to 675 °K, for both phases, on the line shift and Lamb–Mössbauer factor.

Bara and Hryniewicz⁸ prepared their source by first drying an aqueous solution of ⁵⁷CoCl₂ on an aluminum foil. After removal of the water of hydration by heating to 200–300 °C and then further heating in an argon atmosphere at 600 °C they obtained a complicated series of spectra which are not easily interpretable. The complexity was possibly due to the effects of oxidation, clustering, and trapping of the ⁵⁷Co atoms in the surface-oxide film.

In the present work the specimen was a very dilute ⁵⁷Co in aluminum source. With this specimen it was possible to extend the measurements up to near the melting point (660 °C) of aluminum, and thus obtain Mössbauer data on the solid-solution phase in the temperature range 20–642 °C. The real goal was, however, to study the diffusional broadening, which was observed from about 550 °C upwards. The study reported here appears to be the fourth study of diffusional broadening in solids. The first two by Knauer and Mullen were on diffusion of iron in copper⁹ and gold,¹⁰ while the

third was by Lewis and Flinn,¹¹ and was concerned with self-diffusion in bcc iron (this phase was stabilized by the addition of 3-at. % Si).

These previous studies had the benefit of prior reliable diffusion experiments by the tracer technique. This was not the case in this work, since diffusion measurements on the aluminum host have been, and to some degree still are, a controversial subject. Earlier data were in error due to the holdup of the tracer in the surface-oxide film,¹² with the result that absolute diffusion rates were orders of magnitude too low. This problem has been overcome in more recent experiments. Peterson and Rothman¹³ found that the diffusion of a number of nontransition solutes, Zn, Ga, Ge, Cu, Au, Ag, and Sb, in aluminum resembles that of self-diffusion of aluminum. The activation energies are almost identical while the absolute diffusion rates differ at most by a factor of 10.

There remain, however, problems concerning diffusion of transition metals in aluminum; the diffusion of iron in aluminum exemplifies this. Three recent experiments^{12,14,15} gave data points and derived activation energies which do not compare well with each other, indicating that some factor was not completely under control. The result of this work, which is obtained by an alternative method, might thus be of help in explaining the differences.

In the process of converting the measured line broadenings to diffusion constants it is necessary to consider the effects of correlation between atomic jumps. We did this and came to the conclusion that the correlation factor for diffusional line broadening, which was introduced by Knauer,¹⁶ is perhaps given more exactly in our description.

II. THEORY

In the Debye theory the Lamb-Mössbauer factor is given by

$$\phi = e^{-2W}.$$

For $T > \frac{1}{2} \Theta_{\text{eff}}$ the expression for $2W$ can, with a good approximation, be written

$$2W = 6RT/k\Theta_{\text{eff}}^2, \quad (1)$$

where Θ_{eff} is the effective Debye temperature as determined in a Mössbauer experiment, k is the Boltzmann constant, and R is the recoil energy of an unbound emitting nucleus.

In Visscher's simple-impurity theory¹⁷ the quantity Θ_{eff} is related to the Debye temperature Θ_D by

$$\Theta_{\text{eff}} = (M/M')^{1/2} (\gamma'/\gamma)^{1/2} \Theta_D, \quad (2)$$

where M and M' are the masses of the host atom and the impurity atom, while γ and γ' are the spring constants of the host-host and the host-impurity

binding.

The position of the Mössbauer line is dependent on temperature through the second-order Doppler shift

$$\frac{\Delta E}{E} = \frac{U(T_1) - U(T_2)}{2M'c^2}, \quad (3)$$

where E is the energy of the Mössbauer transition, c is the velocity of light, and $U(T_1)$ and $U(T_2)$ are the thermal energies per molecule at the two different temperatures T_1 and T_2 .

When the temperature is high enough, then $U(T) = 3kT$ by the rule of Dulong and Petit. In the case of ^{57}Fe the result is a line shift of -7.32×10^{-4} mm/sec per $^\circ\text{K}$ rise in temperature.

At the very highest temperatures the relaxation time for diffusive jumps of the Mössbauer atoms becomes small in comparison with τ , the mean lifetime of the Mössbauer level. In accordance with Heisenberg's uncertainty principle there is an increased uncertainty in the determination of the transition frequency and thus an increased width of the Mössbauer line.

In order to introduce the various quantities it is helpful to briefly review the theory of tracer diffusion, which as outlined here is especially applicable to diffusion of substitutional impurities in a fcc metal. For a more general review of diffusion see Peterson, Ref. 18.

For a diffusion mechanism in which atomic movement occurs by sudden jumps of equal length r_0 , and with an average jump rate τ_D^{-1} , the diffusion constant D is given by

$$D = (\frac{1}{6} r_0 \tau_D^{-1}) f_C^T, \quad (4)$$

where f_C^T is a factor which describes the correlation in direction between successive jumps of one and the same atom.

For vacancy-assisted self-diffusion f_C^T is a constant which has been calculated and tabulated¹⁸ for the various crystal structures ($f_C^T = 0.78$ for the fcc structure). For diffusion of substitutional impurities in fcc metals the following expression¹⁸ is used:

$$f_C^T = \frac{w_1 + \frac{1}{2} F w_3}{w_1 + w_2 + \frac{1}{2} F w_3}, \quad (5)$$

where the jump rates w_1 , w_2 , and w_3 concern the possible reactions of a Johnson molecule (the complex of an impurity atom and a vacancy at nearest-neighbor separation). Of the 12 possible jumps of the vacancy, one is exchange with the impurity (w_2), four cause a rotation of the Johnson molecule (each of them w_1), and the remaining seven cause dissociation (each of them w_3). F is the fraction of vacancies that after a dissociation jump do not return to the original nearest-neighbor (nn) site.

In the usual description of the temperature de-

pendence of the diffusion constant the activation energy Q is introduced:

$$D = D_0 e^{-Q/kT}. \quad (6)$$

The activation energy for self-diffusion Q_0 (equals the sum of activation energies for vacancy formation and vacancy migration) and the activation energy for impurity diffusion Q_i are connected by

$$Q_i = Q_0 + \Delta E^m - \Delta E^b - C, \quad (7)$$

where ΔE^b is the binding energy of the Johnson molecule and ΔE^m is the difference in activation energies for the w_2 jump and the vacancy jump in the pure crystal, while the term C originates in the temperature variation of f_C^T .

The effects of atomic motion on the Mössbauer spectrum are discussed with reference to the self-correlation formalism of Singwi and Sjölander.¹⁹ The theory is outlined for the emission process (the absorption is perfectly analogous), and according to these authors the energy distribution of emitted radiation is given by

$$I(E) \propto \int dt e^{-i(E-E_0)t/\hbar} e^{-(\Gamma/2\hbar)|t|} G_s(\vec{k}, t), \quad (8)$$

where Γ is the natural width of the excited nuclear level and \vec{k} is the wave vector of the radiation. $G_s(\vec{k}, t)$ is the Fourier transform of the function $G_s(\vec{r}, t)$, which to a good approximation is the self-correlation function that describes how often, on the average, an atom is at position \vec{r} at time t , having begun its motion from $\vec{r}=0$ at $t=0$. Thus

$$G_s(\vec{k}, t) = \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} G_s(\vec{r}, t). \quad (9)$$

In the case of a solid the motion of an atom undergoing diffusion is represented as a succession of sudden jumps between identical vibrational states centered about different lattice sites. Also, it is assumed that vibrational and diffusional motion are uncorrelated, with the result that $G_s(\vec{k}, t)$ can be replaced by $fF(\vec{k}, t)$, the Fourier transform of the self-correlation function for the diffusional motion, multiplied with the Lamb-Mössbauer factor.

It was shown by Knauer¹⁶ that

$$F(\vec{k}, t) = \sum_{n=0}^{\infty} W_n(t) \alpha(\vec{k}), \quad (10)$$

where $W_n(t)$ is the average number of times an atom has made n jumps at time t and $\alpha(\vec{k})$ is the Fourier transform of the one-jump distribution function $h(\vec{r})$. The function $h(\vec{r})$ expresses the average number of times an atom is at position \vec{r} after one jump, the initial position being at $\vec{r}=0$;

$$\alpha(\vec{k}) = \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} h(\vec{r}). \quad (11)$$

If jumps occur by a Poisson process (uncorrelated in time) then the $W_n(t)$ are given by a simple mathematical expression involving τ_D , which also

appears in tracer diffusion [Eq. (4)] as the only parameter. The sum in (10) is in this case easily evaluated. The result is that $F(\vec{k}, t)$ decays exponentially and thus the time Fourier transform in (8) gives a Lorentzian emission line, which is broadened (in energy units) by

$$\Delta E = [1 - \alpha(\vec{k})] 2\hbar\tau_D^{-1}. \quad (12)$$

For a single crystal $h(\vec{r})$ is a sum of δ functions centered at the nn positions and thus $\alpha(\vec{k})=1$ when \vec{k} is a reciprocal-lattice vector. On the other hand, $\alpha(\vec{k}) < 0$ when \vec{k} points to the "center" of a cell in the reciprocal lattice (the minimum of -1 is reached for the simple cubic system but possibly not in other crystal structures). The magnitude of \vec{k} is fixed (by E_0), but since typically $|\vec{k}| = 3(2\pi/r_0)$ it is possible to choose the direction of \vec{k} (direction of observation) so that either of the two cases mentioned above can be realized to a good approximation. In single crystals ΔE should therefore depend strongly on the direction of observation and it should be possible to determine not only the jump frequency (and D) but also the jump direction. This unique feature of the Mössbauer effect has not yet been exploited but it could be very useful in a study of diffusion mechanisms.

For a polycrystal, the phases in the expression for $\alpha(\vec{k})$ average out to give $\alpha(\vec{k})=0$, and only the term $W_0(t)$ is then left in the sum (10). In $W_0(t)$ it is the relaxation time for the first jump of the atom that is of interest. The reciprocal of this time is called $f_C^M \tau_D^{-1}$, introducing the correlation factor f_C^M . It is the correlation in time between successive jumps and not correlation in jump direction that must be considered; therefore $f_C^M \neq f_C^T$, in general.

The main reason for the correlation is that, once the Johnson molecule is formed, there might be more than one exchange jump before dissociation. It is not necessary to study the development in time of such jump reactions but only the outcome, since the rate-controlling step is the formation of the Johnson molecule by the random meeting of an impurity and a vacancy.

By the argument above, the frequency $f_C^M \tau_D^{-1}$ can be expressed as the frequency w_j with which an impurity receives a vacancy to form a Johnson molecule times the probability p_j that a molecule makes one or more exchange jumps before dissociation. The number of Johnson molecules is constant (dynamical equilibrium) and so w_j can be calculated from the breakup rate of existing Johnson molecules; p_j is calculated from the probability that a molecule dissociates before any exchange jumps occur. In this way one obtains

$$\begin{aligned} f_C^M \tau_D^{-1} &= w_j p_j = (7w_3 12p_v) [1 - 7w_3/(w_2 + 7w_3)] \\ &= [7w_3/(w_2 + 7w_3)] (12p_v w_2), \end{aligned} \quad (13)$$

where p_v is the probability that any of the 12 nn sites of the impurity is vacant and, accordingly, $\tau_D^{-1} = 12p_v w_2$. From the final product of Eq. (13) one can therefore see that $f_C^M = 7w_3/(w_2 + 7w_3)$.

The vacancies do not, however, arrive at random since a vacancy that has first left an impurity finds the 12 nn sites of the impurity a rather large target and thus returns within a short time with the probability R (about one-quarter). This fact is taken care of if, in the cases when the vacancy returns, the Johnson molecule is considered not to have dissociated. The consequence of this slight change in the definition of the Johnson molecule is that $w_j p_j$ has to be replaced by $w_j(1 - R)p_j(1 + R)$, correct to first order. Thus the effect of R cancels out, again to first order, and the result is unchanged.

In our new definition the Johnson molecules form at random. This leads to an exponential decay of $W_0(t)$ and thus the emission line and the Mössbauer line have Lorentzian shapes, both of them broadened (in energy units) by

$$\Delta E = 2\hbar f_C^M \tau_D^{-1}, \quad (14)$$

where

$$f_C^M = 7w_3/(w_2 + 7w_3). \quad (15)$$

The discussion above was inspired by the paper of Knauer.¹⁶ However, neither our arguments nor the resulting expressions for f_C^M are identical with his. In the opinion of Knauer, f_C^M should equal the probability that the first jump of the Johnson molecule is a dissociative one. This gives

$$f_C^M = (1 - R)7w_3/(w_2 + 4w_1 + 7w_3), \quad (16)$$

where $R = 0.26$ was found by summing up to three vacancy jumps.

Some details have been ignored so far. First, a fraction $12p_v$ of the impurity atoms are paired with vacancies at $t = 0$, and of those a fraction p_j will jump within a short time. However, if the impurity-vacancy binding energy is not very large, then p_v is small, and the resulting broad component in $I(E)$ cannot be observed because the fractional intensity is low.

We also ignore the changes in hyperfine interactions resulting from the physical presence of the vacancies, which should give an additional broadening of the line. This broadening is small since the vacancy concentration is low and actually the broadening is counteracted by a sort of relaxation when the diffusion is rapid. Simple estimates show that also the additional decrease in the Lamb-Mössbauer factor, caused by the quickly changing strain fields of the migrating defects, can be ignored. Krivoglaz²⁰ has discussed effects of the type mentioned above, and when the defects are interstitial atoms the effects might be observable.

It must be concluded that in fcc metals at high

temperatures the only observable effect of the vacancies on the Mössbauer effect is the diffusional line broadening. A further conclusion is that the use of a source or an absorber specimen leads to the same result, namely, the diffusional jump rate of the Mössbauer atom. This is true since both of the steps in those of the diffusional jumps that can be traced by the Mössbauer effect (formation of the Johnson molecule and exchange jumps) occur after the parent isotope has decayed from ^{57}Co to ^{57}Fe .

III. EXPERIMENTS

The source was prepared in a way which in the first steps was identical to the one used by Bara and co-workers. An aqueous solution of $^{57}\text{CoCl}_2$, the ^{57}Co being carrier free, was dried on an aluminum foil of nominal purity 99.9999%. After removal of the water of hydration the foil was melted in a hydrogen atmosphere and kept in the melted state at 1100 °C for four days. The melt was rolled into an 0.5-mm-thick foil out of which a disk-shaped specimen was cut. The specimen was then heated to 620 °C for four days and air cooled. The activity was 0.6 mCi, corresponding to a concentration of ^{57}Co of about 0.1 ppm.

During the measurement the source was laid on a high-purity Al_2O_3 disk in a furnace of a conventional design. This furnace allowed for a hydrogen protection atmosphere and transmission of radiation through a beryllium window. The temperature was recorded continuously and independently of the temperature regulation. It was found that the temperature could be controlled to within $\pm 2^\circ\text{C}$.

The spectrometer was of the ordinary constant-acceleration type driven in time mode, and the experimental setup was vertical in the transmission geometry, with a vibrating absorber of $\text{K}_4^{57}\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

Twelve spectra were recorded at a series of increasing temperatures. The Mössbauer dips were computer fitted by lines of Lorentzian shape, and this line shape represented even the diffusion broadened dips satisfactorily. The six spectra of the uppermost temperatures are shown in Fig. 1. The convention of negative shifts for source and absorber approaching each other is adopted and 0.405 mm/sec is subtracted from the shifts. In this way the shifts can immediately be compared to those obtained with the use of absorber specimens, in the convention of positive shifts for source and absorber approaching each other and with metallic iron being the reference material.²¹

IV. RESULTS AND DISCUSSION

In addition to the strong solid-solution line a weak line was observed, the two lines being well

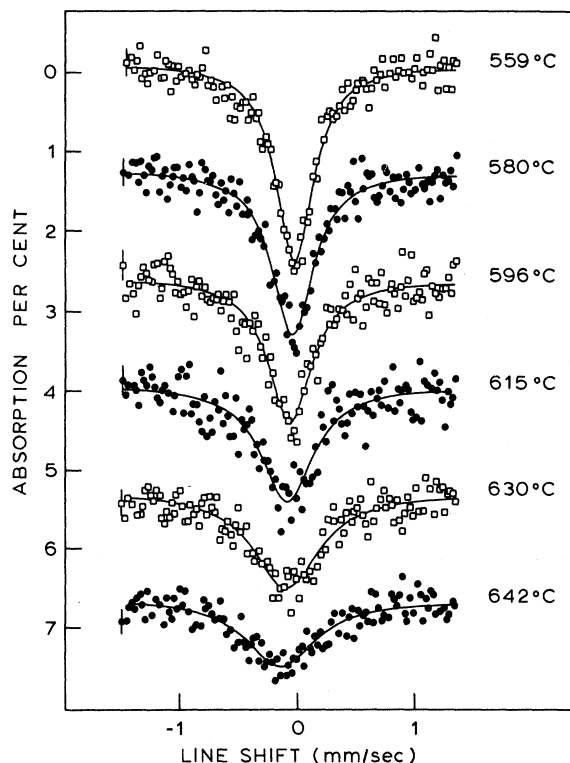


FIG. 1. Mössbauer spectra obtained at the highest temperatures studied.

separated from each other. The presence of the weak line was taken as evidence that about one-tenth of the ^{57}Co atoms were present in a clustered

phase. Above 500°C the weak line vanished, presumably because the clustered phase was dissolved. The resulting change in the number of ^{57}Co atoms in solid solution of about 10% was ignored, since it had little effect on the value of the effective Debye temperature, which is derived from the data.

In Fig. 2 the shift of the solid-solution line was plotted against temperature. The data of this work compare well with those of Nasu and Murakami.⁶ The data of Preston and Gerlach⁷ are probably not very accurate at higher temperatures, since they had to pick out the solid-solution signal by computer fitting. The rather poor result is an example of the difficulty of such an analysis.

The straight line through the points in Fig. 2 has a slope given by the Dulong-Petit rule for the heat capacity. This rule is not valid at low temperatures where the points deviate from the straight line. At high temperatures anharmonicity sets in and causes the small deviations observed in this region.

In Fig. 3 the area of the solid-solution dip, normalized to unity at room temperature, is plotted logarithmically as a function of temperature. The points define a straight line whose slope gives the effective Debye temperature of $(210 \pm 15)^\circ\text{K}$. This is undoubtedly the most reliable determination of Θ_{eff} in the $^{57}\text{FeAl}$ system. Actually, there is good agreement with the value of 220°K , which Nasu and Murakami derived from their data on the temperature shift.

Using the Debye temperature of 428°K for aluminum and Eq. (2), the result is $\gamma'/\gamma = 0.51$. The

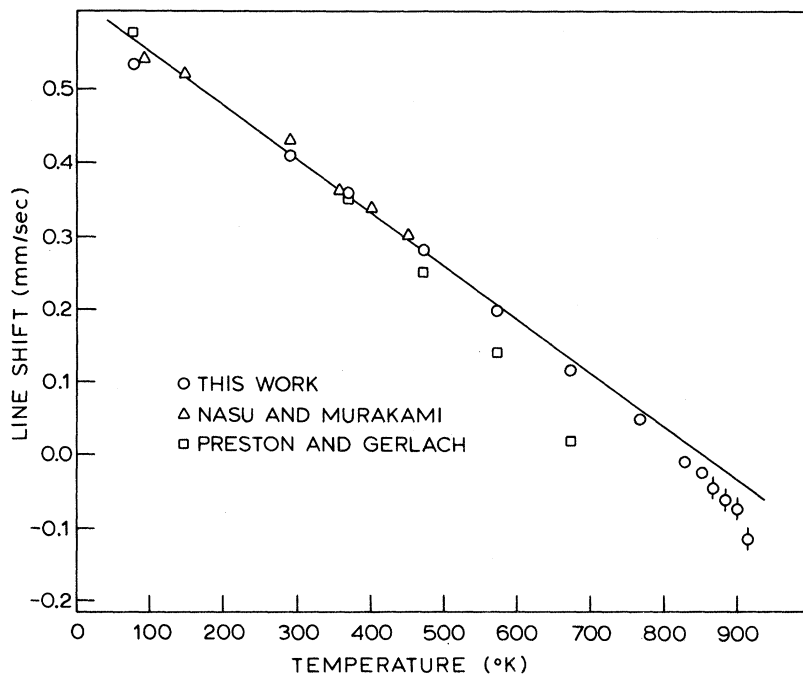


FIG. 2. Second-order Doppler shift. The straight line has the slope $-7.32 \text{ mm/sec}^\circ\text{K}$ as given by the Dulong-Petit rule for the heat capacity.

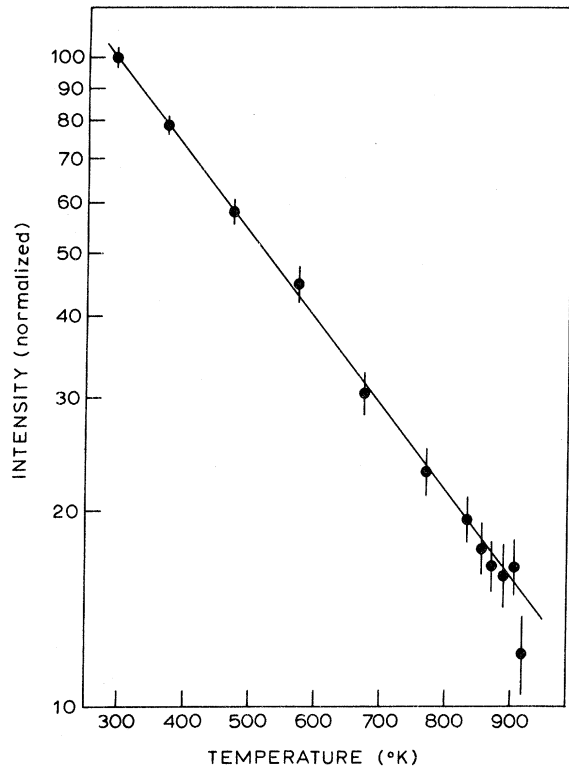


FIG. 3. Decrease in signal strength as function of temperature. The straight line corresponds to an effective Debye temperature of 210 °K.

impurity-host forces are thus significantly weaker than the host-host forces. Those weak forces might be connected with the extremely low solubility of iron in the aluminum host, since experiments by Steyert and Taylor²² on Au, Cu, Ir, Pd, Pt, Rd, and Ti host materials gave γ'/γ values between 0.7 and 1.2. Some of these host materials showed large anharmonic effects, which were just barely detectable for the aluminum host.

The width of the solid-solution line was constant until close to the melting point, where diffusional broadening made it rise steeply from 0.31 to 0.72 mm/sec at 642 °C. The broadenings in excess of

TABLE I. Diffusion data from the experiments shown in Fig. 4.

D_0 (cm ² /sec)	Q_i (eV)	Authors
9.1×10^5	2.68	Hood (Ref. 12)
135	2.00	Alexander and Slifkin (Ref. 14)
?	?	Tiwari and Sharma (Ref. 15)
0.12 ± 0.4	1.4 ± 0.1	This work
Self-diffusion of aluminum		
0.11	1.26	Peterson and Rothman (Ref. 13)

0.31 mm/sec were converted to diffusion constants with the help of Eqs. (4) and (14) and a ratio of correlation factor for tracer diffusion (f_C^T) and line broadening (f_C^M) equal to unity. The diffusion constants are shown in an Arrhenius plot in Fig. 4 together with the most recent data of tracer-diffusion experiments and also a straight line representing self-diffusion of aluminum. The diffusion parameters are collected in Table I.

The diffusion rate of iron in aluminum is obviously about a decade lower than for self-diffusion of aluminum. In view of the line broadening either the frequency for vacancy capture or the probability for exchange jumps before dissociation [w_j and p_j of Eq. (13)] must be smaller than the analogous quantities for self-diffusion, w_j^s and p_j^s . It is not likely that an iron atom, which can form a molecule of positive binding energy with the vacancy, should have a smaller cross section for capture of the freely migrating vacancies, and therefore it follows that $w_j \geq w_j^s$. Accordingly, $p_j < p_j^s$ and it is easily shown that $f_C^M \sim 1$, which again leads to

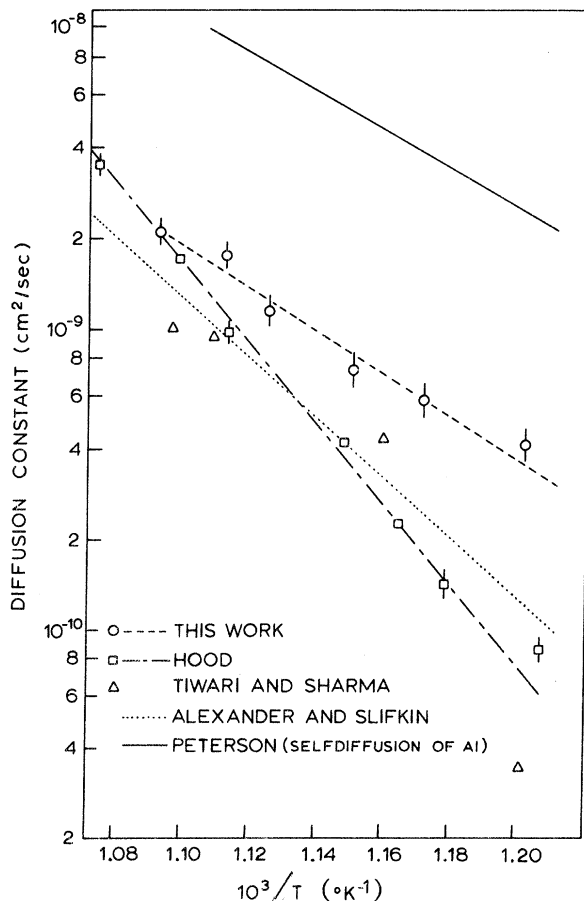


FIG. 4. Most recent determinations of diffusion constants for the diffusion of iron in aluminum.

$f_C^T \approx 1$, and thus the assumption of equally large correlation factors is justified.

The very large Q_i and D_0 values from the tracer experiments are very difficult to accept from intuition. As an example consider the activation energy of 2.68 eV, which according to Eq. (7) gives 1.6 eV for ΔE^m , if $C = 0$, and $\Delta E^b = 0.18$ eV is used. The activation energy of 2.2 eV for the impurity jump into the vacancy is the result. Such a large activation energy for a jump process has not been observed in any other case and most likely the value is incorrect. A similar argument applies to the $D_0 = 9.1 \times 10^5 \text{ cm}^2/\text{sec}$ value.

The results of the tracer experiments are probably in error because of solution trapping. The mechanism is that the implanted iron atoms in the early stage of the diffusion heating will cluster and thus be temporarily trapped. In support of this explanation it can be mentioned that in the preliminary stages of this work it was found that the clustered state ($\text{Fe}_4\text{Al}_{13}$) is very stable and needs a time comparable to the time of diffusion by heating (many hours) to break up.

The trapping is most effective at the lowest temperatures and this explains the biasing of Q_i and D_0 towards higher values and also the discrepan-

cies in the data points at lower temperatures.

The Mössbauer experiment, on the other hand, employed a specimen in thermodynamical equilibrium, since it was kept for many days in the temperature range of rapid diffusion; besides, the Mössbauer effect gave directly a check on clustering reactions. An additional advantage of the Mössbauer effect is that the signal from atoms diffusing rapidly along dislocations, grain boundaries, etc. (pipe diffusion) is smeared out to be unobservable in the temperature range where the true bulk diffusion is studied.

The results of this work make the diffusion of iron in aluminum fall into line with the diffusion of nontransition solutes. This fact, and the consideration above, are in favor of our interpretation of the results. The diffusion of iron in aluminum can thus be represented by the equation

$$D = 0.12 e^{-(1.4 \text{ eV})/kT} \text{ cm}^2/\text{sec}. \quad (17)$$

Further, the second-order Doppler shift is well represented over a wide range of temperatures by the Dulong-Petit rule. The decrease in Lamb-Mössbauer factor with temperature suggests an effective Debye temperature of $(210 \pm 15)^\circ\text{K}$.

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